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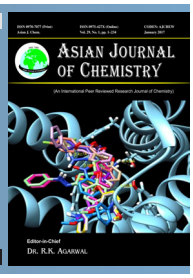

Catalytic Application of Synthesized Capped Silver Nanoparticles for Reduction of *p*-Nitroaniline

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Catalytic activity of synthesized capped silver nanoparticles was performed in the reduction of *p*-phenylene diamine from *p*-nitroaniline in the presence of reducing agent sodium borohydride. The rate of reduction is observed with nanoparticles having different sizes 40, 20 and 40 ± 2 nm. The product obtained in the presence of 20 nm size nanoparticles is in good yield and produced in less time when compared to other nanoparticles. Moreover it is observed that this catalyst showed maximum efficiency at 1 mM concentration and also act as potential recyclable catalyst.

Keywords: Capped silver nanoparticles, Reduction of *p*-nitroaniline, *p*-Phenylene diamine.

INTRODUCTION

It is always fascinating to us that why the nanoparticles are so special and interesting even though these extremely small structures are more complicated than that of their macroscopic counterparts in handling and synthesis. The answer lies in the unique properties possessed by nanostructures. Nanoparticles possess a very high surface to volume ratio. In the manufacturing novel materials, nanotechnology finds a newly emerging field with numerous applications in science. By manipulating size and shape of the particles at nanometre scale (1 to 100 nm) they are used as an efficient catalysts in various industrial applications, in health and daily life [1,2], such as better drug delivery methods [3,4], chemical deposition for environmental pollution cleanup [5,6] medical imaging [7,8] and military purposes [9,10].

EXPERIMENTAL

Synthesis of *Tinospora crispa* extract bio-molecules capped nanoparticles (np1) [11]: *Tinospora crispa* plants are rich in bio-molecules like alkaloids, glycosides, steroids, sesquiterpenoid, aliphatic compound, essential oils, mixture of fatty acids and polysaccharides which have capacity to reduce and stabilize bulk silver into nano silver. The finally cut fresh plant stems of *Tinospora crispa* were dried in a hot air oven at 50-55 °C for one week and then grinded to powder. 100 g of this dried powder was boiled in 200 mL of distilled water for 15-20 min and then cooled. When centrifuged this cooled mixture at 5000 rpm for 10 min a yellow colour supernatant obtained was used for further experiments.

The silver nanoparticles (np1) were synthesized by stirring 40 mL of the supernatant with 200 mL of 1 mM of silver nitrate (purchased from Himedia chemicals) solution at room temperature and the bio-reduced product was monitored periodically by using UV-visible spectrophotometer. The size of the synthesized nanoparticles is found to be 40 nm.

Synthesis of N-(4-Amino-3,5-diphenyl-3*H*-thiazol-2-ylidine)benzamide capped silver nanoparticles (np2) [12]: By stirring slowly 2.5 mL of 10^{-2} M $AgNO_3$ diluted in 75 mL of triply distilled organic-free water with a stabilizer 5 mL of 10^{-2} M *N*-(4-amino-3,5-diphenyl-3H-thiazol-2-ylidine)benzamide (dissolved in hot EtOH) for 10 min at room temperature. 2.5 mL of 10^{-2} M KI was added dropwise until it yields a green yellow AgI colloid, to this 20 mg of $NaBH_4$ was added and stirred for another 20 min. During the stirring, the green-yellow colloidal solution colour changed to nut-brown, then to brown and finally to black. The size of synthesized nanoparticles found to be 20 nm.

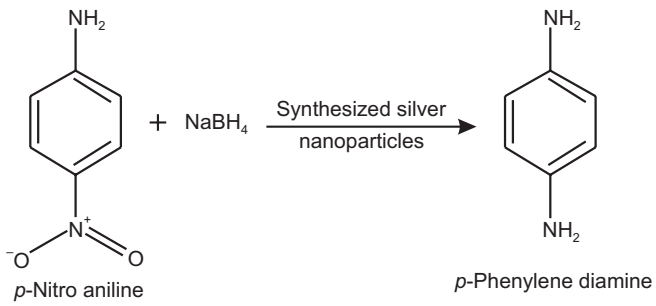
Synthesis of 5-methyl 2-mercapto benzimidazole capped silver nanoparticles (np3) [13]: The solution of $AgNO_3$ (0.1 g, 0.00059 mol) dissolved in 4 mL of deionized water mixed with the solution of 5-methyl 2-mercapto benzimidazole (0.14 g, 0.00089 mol) dissolved in 4 mL ethanol and was stirred continuously for 1 h. To it freshly prepared aqueous $NaBH_4$ (0.04 g, 0.0011 mol, 1 mL) added drop by drop, followed by vigorous stirring for 2 h until colour of the reaction mixture

changed. This indicates the formation of thiol capped silver nanoparticles. The formed capped silver nanoparticles can be isolated by simple filtration followed by washing with ethanol to remove excess capping agent. The size of synthesized nanoparticles is found to be 40 ± 2 nm. These nanoparticles are characterized by UV-visible, FT-IR, SEM, TEM and XRD studies.

Reduction of *p*-nitroaniline by sodium borohydride in presence of nanosilver catalyst: To the 100 µL of 1 mM *p*-nitroaniline, 100 µL of 10 mM $NaBH_4$ and different volumes of silver nanoparticals samples (np1, np2 and np3) of 1, 5 and 10 mM concentrations were added and in order to nullify the dilution effect, different volumes of deionized water were added to the reaction mixture. The chemical reduction of *p*-nitroainilne was monitored by UV-visible spectrophotometer taking freshly prepared solutions in quartz cuvettes. The silver nanoparticles were separated by centrifugation at 11000 rpm and can be reused when washed these particles three to four times with deionized water. These nanoparticles can be reused up to 5 cycles.

RESULTS AND DISCUSSION

The reaction in **Scheme-I** represents the reduction of *p*-nitro aniline to *p*-phenylene diamine with $NaBH_4$ in aqueous solutions in the presence of silver nanoparticles as catalyst. The formation of *p*-phenylene diamine was monitored by UV-visible spectroscopy. A blank experiment was also carried out for the reduction of *p*-nitroaniline with $NaBH_4$ in the absence of silver nanoparticles but the characteristic absorbance of *p*-nitro aniline at 382 nm was slowly decreased after 24 h.



Scheme-I

When the reaction was performed in the presence of above synthesized silver nanoparticles, the characteristic absorbance of *p*-nitroaniline at 382 nm showed a progressive decrease and the appearance of a new absorption peak at 310 nm as showed in Fig. 1. This indicates that reduction of *p*-nitroaniline to *p*-phenylenediamine in the presence of $NaBH_4$ is accelerated by using the silver nanoparticles. Since this reagent was used in large excess with respect to *p*-nitroaniline in the reaction, rate is independent of the concentration of $NaBH_4$ which implies that the chemical reduction reaction follows first-order kinetics.

When comparing the rates of reaction of the catalyst np1, np2 and np3, it is observed that the rate is high for np2 sample produced from 1 mM of $AgNO_3$ medium than the silver sample produced from 5 mM of $AgNO_3$ and slow when using the silver sample produced from 10 mM of $AgNO_3$ as a catalyst. As the

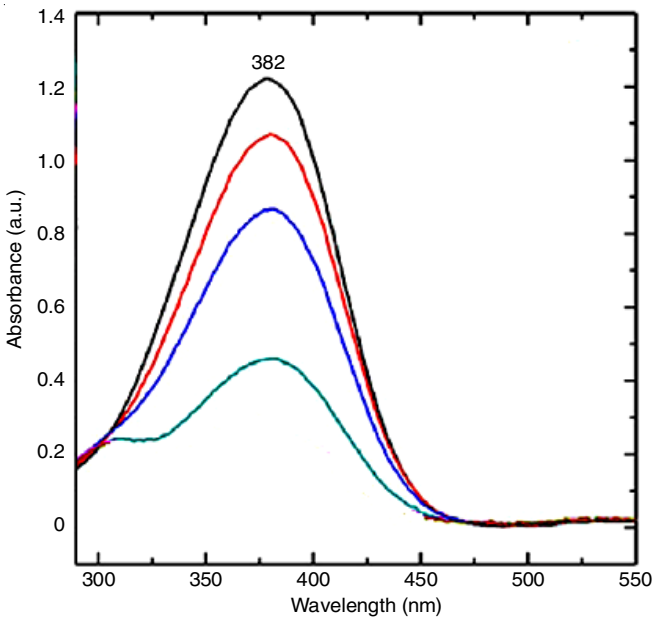


Fig. 1. UV-visible spectra for the successive chemical reduction of *p*-nitroaniline with $NaBH_4$ catalyzed by reused silver nanoparticles

particle sizes of np1 and np3 samples are same (40 nm), the rates of reaction are found approximately equal. The percentage conversion of *p*-nitro aniline to *p*-phenylene diamine were about 96.1, 89.8 and 76.6 % in the presence of the silver sample obtained from 1, 5 and 10 mM $AgNO_3$, respectively.

In this study, as the number of silver nanoparticles maintained in all reaction mixtures are approximately same since the variation in reaction rate or catalytic efficiency depends on the available surface area. In the present reduction, the electron transfer occurs from BH_4^- to *p*-nitro aniline *via* silver nanoparticles. It was observed that large silver nanoparticles have more steric interactions with BH_4^- and *p*-nitro aniline compared to small like gold nanoparticles [14,15] because more number of molecules were wrapped on the surface of large silver nanoparticles with respect to small silver nanoparticles.

Therefore, the reaction rate is fastest in small (20 nm) silver nanoparticles produced from 1 mM $AgNO_3$ with respect to the large silver nanoparticles produces from 5 mM and 10 mM $AgNO_3$ but in all cases the reduction is completed in less than 2 h. The reason for silver nanoparticles produced from 10 mM $AgNO_3$ showed slow reaction rate compared to the silver nanoparticles produced from 5 mM $AgNO_3$ is, it consists of mixture of shapes of nanoparticles, such as quasi-spheres, triangles and rods has lower effective catalytic surface area than the silver sample resulting from 5 mM $AgNO_3$ which consist only quasi-spheres. This is not sufficient to explain the exact reason for these variations in the reaction rates, but to understand exact catalytic process further investigations need to be carried out. The 1mM silver nanoparticles catalyst used as precursor requires less than 1 h time (Table-1) for the complete reduction of *p*-nitro aniline to *p*-phenylene diamine, which is lower or slightly higher than the gold nanoparticles synthesized from the chemical routes and also the earlier used chemicals (gold(III) chloride) are costly when compared to present silver nitrate catalysts [14-16].

TABLE-1
CATALYTIC EFFICIENCY OF SILVER NANOPARTICLES WITH DIFFERENT CORE SIZES DETERMINED IN THIS STUDY

Ag-NPs	Particle core size (nm)	Time for complete the reduction (min)	*p*-Nitroaniline conversion (%)
np1	40	85	76.2
np2	20	55	97.1
np3	40±2	88	74.5

It is further examined for the recyclability of these nanoparticles. Fig. 2 shows the reusable catalytic properties for the reduction of *p*-nitro aniline with $NaBH_4$ in the presence of silver nanoparticles obtained from 1 mM $AgNO_3$. It is found that, even after 5 recycling reactions, the conversion rate reaching about 88 %. Thus, the silver nanoparticles synthesized were potent recyclable nanocatalyst for the industrial applications.

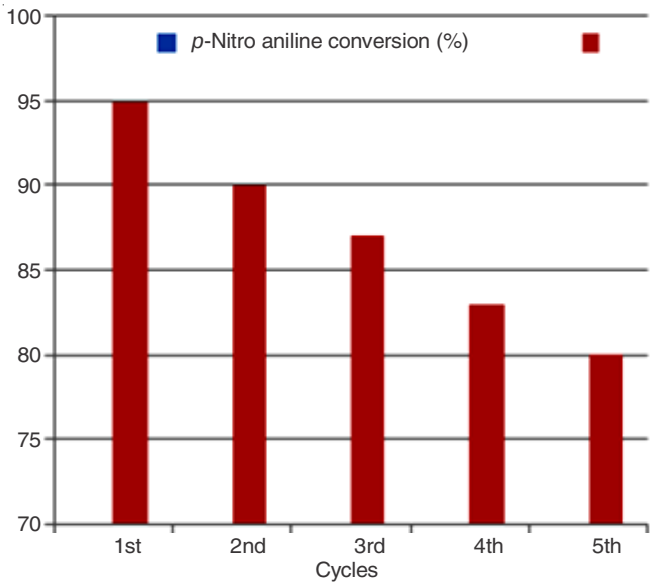


Fig. 2. Recyclability of the silver nanoparticles (np2) obtained from 1 mM $AgNO_3$ as a catalyst for the reduction of *p*-nitro aniline with $NaBH_4$

Conclusion

Capped silver nanoparticles np1, np2 and np3 of different sizes 40 nm, 20 nm, 40 ± 2 nm respectively are synthesized and employed as catalyst in the reduction of *p*-nitro aniline with $NaBH_4$ to *p*-phenylene diamine. It is observed that the speed of reaction was fast when using the np2 sample compared to the np1 and np3 samples due to their size, as particle size decreases surface area increases. It is also observed that the rate of reaction is fast with np2 produced from 1 mM of $AgNO_3$ medium in comparison with the silver sample produced from 5 mM and 10 mM of $AgNO_3$ as a catalyst. This is because the nanoparticles of size 20 nm produced from 1 mM of $AgNO_3$ medium have more effective surface area and posses less steric hindrance with *p*-nitro aniline and $NaBH_4$ when compared to nanoparticles of size 20 nm produced from 5 mM and 10 mM due to their shape. The recyclability of nanoparticles of size 20 nm produced from 1 mM of $AgNO_3$ shows it is potential recyclable catalyst for industrial applications.

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